

On the Galilean transformation of the few-electron wave functions.

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Abstract

The Galilean transformations of the few-electron atomic wave functions are considered. We discuss the few-electron wave functions constructed in the model of independent electrons as well as the truly correlated (or highly accurate) wave functions. Results of our analysis are applied to determine the probability of formation of the negatively charged tritium/protium ions during the nuclear $(n, {}^3\text{He}; t, p)$ -reaction of the helium-3 atoms with thermal/slow neutrons.

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The general formulas for the Galilean transformation of the non-relativistic, single-particle wave function $\Psi(\mathbf{r}, t)$ are well known since the middle of 1920's (see, e.g., [1]). If $\Psi(\mathbf{r}, t)$ is such a wave function written in the reference frames which are at rest, then the corresponding wave function $\Psi'(\mathbf{r}', t)$ in the moving frames takes the form

$$\Psi'(\mathbf{r} - \mathbf{V}t, t) = \Psi(\mathbf{r}, t) \exp\left[\frac{im}{\hbar}(-\mathbf{V} \cdot \mathbf{r} + \frac{1}{2}V^2t)\right] \quad (1)$$

or

$$\Psi'(\mathbf{r}, t) = \Psi(\mathbf{r} + \mathbf{V}t, t) \exp\left[\frac{im}{\hbar}(-\mathbf{V} \cdot \mathbf{r} - \frac{1}{2}V^2t)\right] \quad (2)$$

From Eq.(2) one easily finds the following transformation formulas for the non-relativistic wave function of an arbitrary few-particle system. To avoid analysis of very general quantum systems in this study we restrict ourselves to the consideration of few-electron atomic systems only. Here and everywhere below by an 'atomic system' we mean the bound few-electron system with one very heavy center which also has a positive electric charge Qe . The forces of electric attraction between nucleus and electrons bind this system together. The competing forces of electric repulsion between electrons decrease the final value of binding energy, but they are relatively small.

The general formulas for the Galilean transformations of the actual few-electron (atomic) wave function follow from formulas, Eqs.(1) - (2). For such systems one finds a number of advantages to write all formulas in atomic units, where $\hbar = 1, e = 1, m_e = 1$. In this units for the N -electron system we have

$$\Psi'(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \Psi(\mathbf{r}_1 + \mathbf{V}t, \dots, \mathbf{r}_N + \mathbf{V}t, t) \exp\left[i(-\mathbf{V} \cdot \sum_{i=1}^N \mathbf{r}_i - N\frac{1}{2}V^2t)\right] \quad (3)$$

This formula is correct for any atomic system which contains N independent (or quasi-independent) electrons. By approximating the actual N -electron wave functions by the trial functions constructed in the model of quasi-independent electrons one can show that the formula, Eq.(3), is correct in the general case, i.e. when all electron-electron correlations are included.

In reality, we need the formulas for the Galilean transformations of the N -electron wave functions in the limit $t \rightarrow 0$. This limit corresponds to the sudden approximation [2], [3] for few-electron atomic systems. For instance, all processes, decays and reactions in atomic nuclei proceed significantly faster than usual electron transitions in atoms. Therefore, the

sudden approximation can be applied to determine the probabilities of the electron-electron transitions during nuclear reactions in atoms. In many cases it is important to know the probabilities to form various ‘final atomic states’ after some fast nuclear process in the atomic nucleus. The ‘incident’ atomic state is usually known. In many cases the newly created nuclei (or ‘nuclear fragments’) are rapidly moving after the nuclear reaction and/or decay. In such cases one finds numerous advantages to determine the final state probabilities by using the moving frames with the origin located at the atomic nucleus. In these frames all atomic electrons suddenly take the speed $-\mathbf{V}_n$, where the subscript n means the nucleus. Now, the formula for the sudden (Galilean) transformation of the non-relativistic wave function of a N -electron atomic system takes the form

$$\Psi'(\mathbf{r}_1, \dots, \mathbf{r}_N) = \exp(i\mathbf{V}_n \cdot \mathbf{r}_1 + i\mathbf{V}_n \cdot \mathbf{r}_2 + \dots + i\mathbf{V}_n \cdot \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (4)$$

This formula is written in the form which can directly be used for an arbitrary N -electron atom with independent and/or quasi-independent electrons. In such cases the wave function depends upon the N electron-nuclear $r_i = r_{in}$ coordinates (scalars) only. However, all actual, few-electron wave functions are truly correlated, i.e. they explicitly depend upon both the electron-nuclear $r_i = r_{in}$ and electron-electron r_{ij} coordinates, which are also called the correlation coordinates. Formulas for the Galilean transformations of the electron-electron coordinates r_{ij} can be obtained from their definitions. Indeed, according to the definition of r_{ij} we can write the following identities $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = |\mathbf{r}_i - \mathbf{r}_n - (\mathbf{r}_j - \mathbf{r}_n)| = |\mathbf{r}_i - (\mathbf{r}_n - \mathbf{V}\delta t) - [\mathbf{r}_j - (\mathbf{r}_n - \mathbf{V}\delta t)]| = r_{ij}$, where δt is infinitely small. This means that the electron-electron coordinates r_{ij} does not depend upon \mathbf{V} , i.e. it does not change during the sudden motion of the nucleus. It follows from here that the sudden Galilean transformations of the truly correlated wave function are also described by the same formula, Eq.(4).

The formula, Eq.(4), can be applied to determine the probability of formation of the tritium ${}^3\text{H}^-$ ion during the reaction of the ${}^3\text{He}$ nuclei with slow/thermal neutrons [4]



in the two-electron helium-3 atom. In the reaction Eq.(5) the notations ${}^3\text{H}$ and ${}^1\text{H}$ stand for the tritium nucleus (or t nucleus) and protium (or p nucleus). The reaction, Eq.(5), is of great interest for the burning of the high-dense deuterium plasmas [5] ($\rho \geq 100 \text{ g} \cdot \text{cm}^{-3}$ (see also [6])). The reaction, Eq.(5), in the two-electron ${}^3\text{He}$ atom and one-electron ${}^3\text{He}^+$ ion

was considered in our earlier studies [7], [8]. The cross-section σ of this nuclear reaction for thermal neutrons with $E_n \approx 0$ is very large $\sigma_{max} \approx 5330 \cdot 10^{-24} \text{ cm}^2$ (or 5330 *barn*) [9]. The velocities of the two nuclear fragments formed in the reaction, Eq.(5), with thermal neutrons are $v_t \approx 1.59632 \text{ a.u.}$ and $v_\alpha \approx 4.78797 \text{ a.u.}$ for the tritium and protium nuclei, respectively. In this study all particle velocities are given in atomic units, where $\hbar = 1, m_e = 1, e = 1$ and the unit of atomic velocity is $v_e = \alpha c \approx \frac{c}{137} \approx 2.1882661 \cdot 10^8 \text{ cm} \cdot \text{sec}^{-1}$. Here and everywhere below c is the speed of light and $\alpha = \frac{e^2}{\hbar c}$ is the dimensionless fine structure constant. This ‘atomic velocity’ v_e is the velocity of the $1s$ -electron in the hydrogen atom with the infinitely heavy nucleus $^\infty\text{H}$. It is clear that in atomic units $v_e = 1$.

Let us evaluate the probabilities of formation of the negatively charged tritium and protium ions. In other words, we want to determine the probabilities of formation of the two-electron $^3\text{H}^-$ and $^1\text{H}^-$ ions during the nuclear reaction, Eq.(5), in the two-electron ^3He atom. According to the theory of sudden approximations and in respect with Eq.(3) such a probability of formation of the tritium ion ($^3\text{H}^-$ or T^-) is written in the form $P_{if} = |A_{if}|^2$, where A_{if} is the probability amplitude which is written in the form

$$A_{if} = \langle \Phi_{\text{T}^-}(\mathbf{r}_1, \mathbf{r}_2) | \Psi'_{\text{He}}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \langle \Phi_{\text{T}^-}(\mathbf{r}_1, \mathbf{r}_2) | \exp(i\mathbf{V}_t \cdot \mathbf{r}_1 + i\mathbf{V}_t \cdot \mathbf{r}_2) \Psi_{\text{He}}(\mathbf{r}_1, \mathbf{r}_2) \rangle \quad (6)$$

where V_t is the speed of the tritium nucleus after the reaction, Eq.(5). In other words, the probability amplitude is the overlap integral between the tritium ion and helium-3 wave functions, but the wave function of the helium-3 atom must be taken in the moving reference frames.

In the incident and final wave functions we can separate three internal variables r_{32}, r_{31}, r_{12} (or relative coordinates $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = |\mathbf{r}_{ij}|$) from other six ($3 + 3$) variables which correspond to the translational and rotational degrees of freedom of the whole three-body system. Here and everywhere below the notations 1 and 2 mean the electrons, while the notation/index 3 stands for the central (heavy) nucleus. In atoms with one heavy nucleus the internal coordinates coincide with the interparticle, or relative coordinates. In general, the expression for the probability amplitude A_{if} , Eq.(6), is reduced to the following form

$$A_{if} = \int \int \int \mathcal{Y}_{LM}^{\text{T}^-}(\mathbf{r}_{31}, \mathbf{r}_{32}) \Phi_{\text{T}^-}(r_{32}, r_{31}, r_{21}) \exp(i\mathbf{V}_t \cdot \mathbf{r}_{32} + i\mathbf{V}_t \cdot \mathbf{r}_{31}) \times \\ \mathcal{Y}_{LM}^{\text{He}}(\mathbf{r}_{31}, \mathbf{r}_{32}) \Psi_{\text{He}}(r_{32}, r_{31}, r_{21}) r_{32} r_{31} r_{21} dr_{32} dr_{31} dr_{21} \quad (7)$$

for the tritium $^3\text{H}^-$ (or T^-) ion. The notations $\mathcal{Y}_{LM}^{\text{T}^-}(\mathbf{r}_{31}, \mathbf{r}_{32})$ and $\mathcal{Y}_{LM}^{\text{He}}(\mathbf{r}_{31}, \mathbf{r}_{32})$ used in this equation designate the corresponding bi-polar harmonics [10] (see also [11]). They are

taking care about non-zero angular momenta of the incident and final atomic species. It should be mentioned here that the negatively charged hydrogen ion H^- has only one bound $1^1S(L=0)$ -state. Also, in this study we restrict ourselves to the case when the incident 3He atom was in its ground $1^1S(L=0)$ -state. In this case all bipolar harmonics in Eq.(7) equal unity and the probability amplitude, Eq.(7), takes the form

$$A_{if} = \int \int \int \Phi_{T^-}(r_{32}, r_{31}, r_{21}) j_0(V_t \cdot r_{32}) j_0(V_t \cdot r_{31}) \Psi_{He}(r_{32}, r_{31}, r_{21}) r_{32} r_{31} r_{21} dr_{32} dr_{31} dr_{21} \\ = \frac{1}{V_t^2} \int \int \int \Phi_{T^-}(r_{32}, r_{31}, r_{21}) \sin(V_t \cdot r_{32}) \sin(V_t \cdot r_{31}) \Psi_{He}(r_{32}, r_{31}, r_{21}) r_{12} dr_{32} dr_{31} dr_{21} \quad (8)$$

where V_t is the speed of the tritium nucleus after the nuclear reaction in the 3He atom.

The wave functions of the ground $1^1S(L=0)$ -states in the two-electron H^- ion and He atom are usually approximated with the use of highly accurate variational expansion written in the relative/perimetric coordinates r_{32}, r_{31} and r_{21} or u_1, u_2, u_3 (more details can be found, e.g., [12]). The most advanced of such expansions is the exponential variational expansion in the relative coordinates. It takes the following form (for the bound $S(L=0)$ -states in the two-electron systems):

$$\psi(r_{32}, r_{31}, r_{21}) = \frac{1}{\sqrt{2}} [1 + (-1)^\kappa \hat{P}_{12}] \sum_{i=1}^N C_i \exp(-\alpha_i r_{32} - \beta_i r_{31} - \gamma_i r_{21}) \chi(1, 2) \quad (9)$$

where C_i are the linear variational coefficients, \hat{P}_{12} is the permutation of the two identical particles (electrons 1 and 2) and N is the total number of terms in the trial function $\psi(r_{32}, r_{31}, r_{21})$ which is an accurate approximation of the actual wave function $\Psi(r_{32}, r_{31}, r_{21})$. In Eq.(9) the notation $\chi(1, 2)$ stands for the two-electron spin function. For the singlet states $\chi(1, 2) = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$ and $\kappa = 0$ in Eq.(9). The total energies obtained for the ground 1^1S -states of the H^- ion and He atom with the use of Eq.(9) can be found in Table I. The wave functions, Eq.(9), are used in calculations of the probability to form the bound tritium ion $^3H^-$.

For the tritium ion $^3H^-$ the probability amplitude A_{if} is written as the double sum of the following three-particle integrals

$$B_{0;0;1}^{(00)}(\alpha, \beta, \gamma; V_t) = \frac{1}{V_t^2} \int \int \int \exp(-\alpha r_{32} - \beta r_{31} - \gamma r_{21}) \sin(V_t \cdot r_{32}) \times \\ \sin(V_t \cdot r_{31}) r_{12} dr_{32} dr_{31} dr_{21} \quad (10)$$

Theory of these integrals was developed in [13]. In particular, it was shown in [13] that such

an integral is reduced to the following double sum (here we apply the Cauchy formula)

$$B_{0;0;1}^{(00)}(\alpha, \beta, \gamma; V) = \sum_{\kappa=0}^{\infty} \frac{(-1)^{\kappa} V^{2\kappa}}{(2\kappa + 2)!} \sum_{\mu=0}^{\kappa} C_{2\kappa+2}^{2\mu+1} \Gamma_{2\mu+1;2\kappa-2\mu+1;1}(\alpha, \beta, \gamma) \quad (11)$$

where C_n^k is the binomial coefficient, i.e. the number of combinations from n by k ($n \geq k$), and $\Gamma_{k;l;n}(a, b, c)$ is the basic three-particle integral defined in [13]. This formula allows one to determine the probability to form the bound T^- (or ${}^3H^-$) and ${}^1H^-$ ions during the nuclear reaction, Eq.(5), in the two-electron 3He atom. For instance, by using the approximate one-term wave functions for the ground state in the helium atom and hydrogen ion given in Table II of Ref.[7] we have found that the probability to form the bound T^- (or ${}^3H^-$) ion in the reaction Eq.(5) is $\approx 0.77048798 \%$ (probability amplitude is ≈ 0.87777445). Such a large probability of the T^- ion formation means that these ions formed in the reaction, Eq.(5), can easily be detected in modern experiments. Analogous probability for the negatively charged protium ion is only $\approx 2.391074 \cdot 10^{-5} \%$ (probability amplitude is $\approx 0.48898613 \cdot 10^{-3}$), i.e. it is significantly smaller. This illustrates a very sharp dependence of the final state probabilities upon the final velocity of the atomic particle (for $V \geq 1$) [2], [7].

It is interesting to note that we can also use the formula, Eq.(11), in the case $V = 0$. This case corresponds to the β^- decay of the ${}^3H^-$ ion into the two-electron 3He atom. The corresponding probability obtained with our one-term wave functions is $\approx 23.893045 \%$ (probability amplitude is ≈ 0.4880502483). These amplitude and final probability are very close to our earlier prediction made in 1998. Analogous calculations with the use of three-term variational wave functions (with the carefully optimized non-linear parameters) for the H^- ion and He atom gives the following probabilities: 22.065318% (β^- decay), 0.879736% (${}^3H^-$ ion formation) and $5.72186 \cdot 10^{-5} \%$ (${}^1H^-$ ion formation). The corresponding variational three-term energies for the ${}^\infty H^-$ ion and ${}^\infty He$ atom are $-0.527665299440825 \text{ a.u.}$ and $-2.90363883557241 \text{ a.u.}$, respectively (compare with the energies from Table I).

Note that our variational few-term wave functions for the both atomic systems (H^- ion and He atom) with carefully optimized non-linear parameters are the best functions in their class. Nevertheless, it is very interesting to check our predictions by using variational wave functions for the H^- ion and He atom with significantly larger number of terms, e.g., the trial wave functions from Table I. In actual calculations with such wave functions we have found an additional problem related with the use of the non-orthogonal basis sets in calculations of the overlap integrals which include the two different wave functions. This problem was never

discovered in earlier studies where different expectation values were computed for the same systems. In such cases the bound state wave functions were exactly identical for the ‘incident’ and ‘final’ state. The situation changes drastically, if we consider the overlap integrals of two different wave functions written in the non-orthogonal basis sets. To illustrate the problem, let us suppose that we have changed the order of basis vectors in the second wave function in the overlap. It does not change the norm of this (i.e. second) wave function, but numerical value of the overlap integral can be changed substantially, since the transformation which connects these two non-orthogonal basis sets is not unitary (or orthogonal). Briefly, this means that we cannot predict the right order of basis functions (in the two approximate wave functions) which is only appropriate for calculations of the final state probabilities. At this moment we are trying to solve this interesting problem and develop the new, reliable method for accurate computations of the final state probabilities.

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TABLE I: The total energies E of the ground $1^1S(L = 0)$ -states in the negatively charged hydrogen ion ${}^\infty\text{H}^-$ and ${}^\infty\text{He}$ atom (in atomic units). K is the total number of basis functions used.

K	$E({}^\infty\text{H}^-)$					$E({}^\infty\text{He})$			
3500	-0.527751	016544	377196	590213		-2.903724	377034	119598	030965
3700	-0.527751	016544	377196	590333		-2.903724	377034	119598	030983
3840	-0.527751	016544	377196	590389		-2.903724	377034	119598	030995
4000	-0.527751	016544	377196	590446		-2.903724	377034	119598	031033